Highly efficient tetranuclear ZnII2LnIII2 catalysts for the Friedel-Crafts alkylation of indoles and nitrostyrenes

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Highly Efficient Tetranuclear $Zn^{II}_2Ln^{III}_2$ Catalysts for the Friedel–Crafts Alkylation of Indoles and Nitrostyrenes

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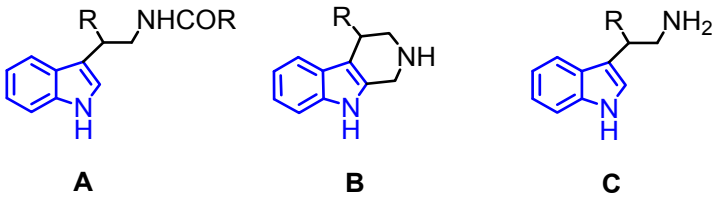
Abstract: We demonstrate for the first time the high efficacy of tetranuclear $Zn^{II}_2Ln^{III}_2$ coordination clusters (CCs) as catalysts for the Friedel–Crafts (FC) alkylation of indoles with a range of *trans*-β-nitrostyrenes. The reaction proceeds in good to excellent yields (76%–99%) at room temperature with catalyst loadings as low as 1.0 mol %.

Keywords: Friedel–Crafts alkylation; Zn/**4f**; coordination clusters

1. Introduction

The Friedel–Crafts (FC) reaction of aromatic compounds with electron-deficient alkenes is used widely in synthetic organic chemistry [1,2]. The reaction between indole and β-nitrostyrene is important as it gives access to indole-based alkaloids such as melatonin analogues (**A**), 1,2,3,4-tetrahydro-β-carbolines (THBCs, (**B**)), and "triptans" (**C**) (Scheme 1) [3,4].



Scheme 1. Versatile intermediates in organic synthesis derived from Indolylnitroalkanes.

Nitroalkenes have received considerable attention as active Michael acceptors [5] because the nitro derivatives can be transformed into amino compounds with a variety of different functionalities [6–10]. For the reaction between indole and β-nitrostyrene, various catalytic systems have been proposed. These include hydrogen-bond-based compounds [11–16] such as thiourea [11,14,15,17–20], phosphoric acid [16], silanediols [21,22], sulfamic acid [23] and 2,6-bis(amido)benzoic acid [24]; metal based compounds [25–41] such as Al^{III} [25,39], Cu^{II} [26–30,41], Zn^{II} [31–35,40,42], Fe^{III} [36], Pd^{II} [37], Rh^{II} [43,44] and SmI_3 [38]; and heterogeneous systems including metal organic frameworks, [45,46] nano n-propylsulfonated γ-Fe_2O_3 (NPS-γ-Fe_2O_3) [47] and zeolite HY [48]. However efficient metal catalytic systems for this transformation are very rare. Du [49–53] developed an efficient catalyst containing bisoxazolines and bisimidazolines-$Zn(OTf)_2$. Wang reported the involvement of a dimeric Cu^{II} coordination cluster (CC) and piperidine as a catalyst for reactions between aromatic nitroalkenes and ortho-substituted indoles [41]. However, some of

the reported protocols have drawbacks such as high catalyst loading, long reaction time, the need for additives, low temperature (0 to −20 °C) and multi-step designed ligands, thus limiting their practical applications.

In **3d/4f** chemistry, only a few polynuclear CCs have been successfully used as homogenous catalysts [54–56]. We recently initiated a project on the synthesis of **3d/4f** CCs stabilized by the Schiff base organic ligand H2L [(*E*)-(2-hydroxy-3-methoxybenzylidene-amino)phenol], that would display catalytic properties [57–59]. We also reported the synthesis and characterisation of a series of isoskeletal [60] tetranuclear $Zn^{II}_2Ln^{III}_2$ CCs formulated as $[Zn^{II}_2Ln^{III}_2L_4(NO_3)_2(DMF)_2]$ (**1Ln**) where Ln is Y (**1Y**), Sm (**1Sm**), Eu (**1Eu**) Gd (**1Gd**), Dy (**1Dy**), Tb (**1Tb**) and Yb (**1Yb**) possessing a defect dicubane topology (Figure 1). These compounds can be synthesized quantitatively in two steps, up to multigram scale and are air stable for a few months. We showed that these bimetallic species remain intact in organic and aqueous solutions, by ESI-MS studies, EPR studies for **1Gd** and NMR studies for **1Y** analogues. This precise topology shows that the Zn and the Ln centres are very close (approximately 3.3 Å), permitting both metals to coordinate to the substrates and promote the coupling reaction. Compounds **1Y** and **1Dy** showed high efficiency as catalysts, at room temperature, with low catalytic loadings in FC alkylation of indole with aldehydes leading to bis-indolylmethane derivatives [59]. A study of the suitability of **1Ln** as catalysts in FC alkylation of indole with nitrostyrene is presented herein.

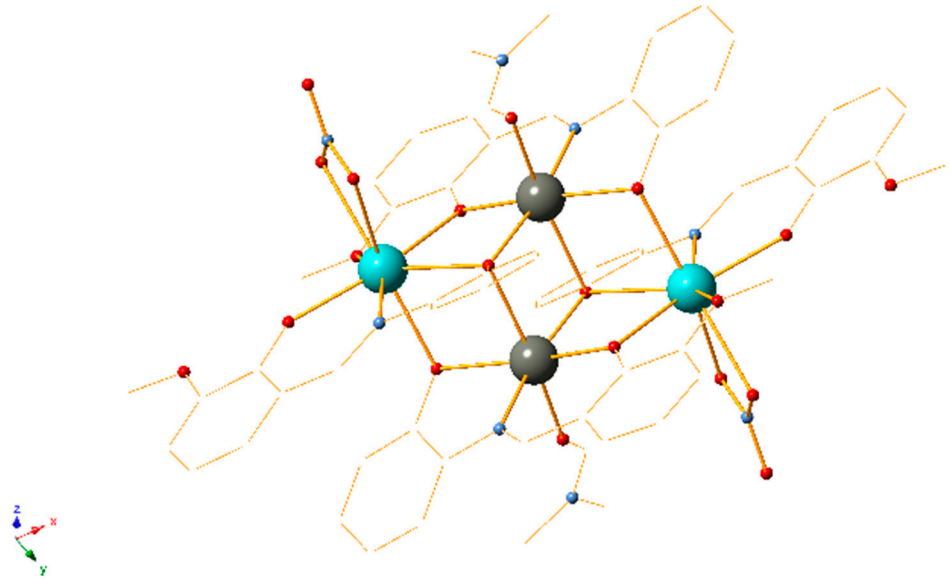


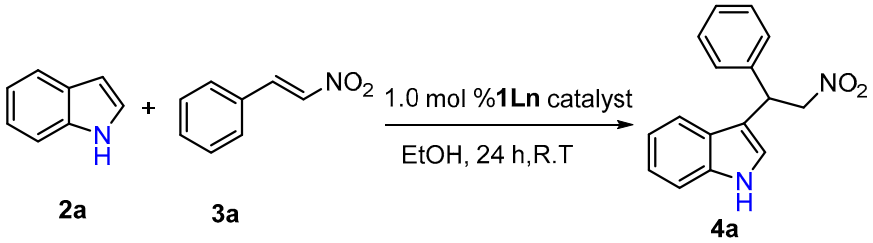
Figure 1. Molecular structure of **1Ln**. Colour code: Zn^{II}: grey; Ln^{III}: light blue; O: red; N: blue. C and H atoms are omitted for clarity.

2. Results

The first step was to optimize the reaction conditions for the alkylation of indole. We screened several reaction parameters, such as the use of different catalysts (Table 1, entries 1–9), solvents (Table 1, entries 10–14), temperature (Table 1, entries 15–17) and catalyst loading (Table 1, entries 18–20). We studied the reaction between indole (0.50 mmol) **2** and nitroalkene (0.50 mmol) **3** in EtOH at room temperature and a catalyst loading of 1.0 mol % (Table 1 entries 1–9). A blank experiment in the absence of the **3d/4f** CCs catalyst showed no conversion (Table 1, entry 1) and very low conversions were obtained in the presence of Dy or Zn salts (Table 1, entries 2–3). The reactions with **1Dy** and **1Y** after 24 h show very high yields, 99% and 94%, respectively. (Table 1, entries 4–5). Other catalysts such as **1Eu**, **1Gd**, **1Nd** and **1Tb** showed lower yields (Table 1, entries 1–6). Therefore, **1Dy** was the best choice for this FC reaction. We then decided to identify the influence of the solvent on the catalytic performance. Our catalyst showed high activity in ethanol with 99% yield of the desired product **4a**

(Table 1, entry 4). Solvents such as THF, water, acetonitrile and *N*,*N*′-dimethylformamide (DMF) had a negative influence on the catalytic activity; therefore, ethanol was the best choice for further studies. At room temperature, the yield of **4a** was 99%, but only 5% at 0 °C. Lower yields were obtained at 60 °C (Table 1, entry 18), so the following reactions were made at this temperature. As shown in Table 1, it was sufficient to use a catalyst loading of 1.0 mol % to obtain a yield up to 99% (Table 1, entry 4). An increase of the catalyst loading from 1.0 mol % to 5 mol % led to a remarkable decrease in the yield of the desired product **4a** (Table 1, entries 19–20). This finding can be explained due to the low solubility of the catalyst. Further, a decrease in the catalyst loading to 0.5 mol % also showed lower yield of the desired product **4a** (Table 1, entry 18). Therefore, we used 1.0 mol % **1Dy** in ethanol at room temperature for further experiments.

Table 1. Optimization of the Friedel–Crafts Alkylation of Indole **2a** with *trans*-β-Nitrostyrene **3a** Catalyzed by **1Ln** Complexes [a].

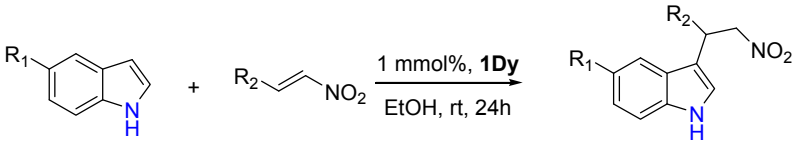


Entry	Catalyst	Yield (%) [b]
1	none	0
2	Dy $(OTf)_3$	8
3	Zn $(OTf)_2$	20
4	**1Dy**	99
5	**1Y**	94
6	**1Eu**	55
7	**1Gd**	30
8	**1Nd**	12
9	**1Tb**	24
10	**1Dy** (Toluene)	30
11	**1Dy** (Water)	0
12	**1Dy** (THF)	0
13	**1Dy** (Acetonitrile)	0
14	**1Dy** (DMF)	5
15	**1Dy** (−30 °C)	0
16	**1Dy** (0 °C)	5
17	**1Dy** (60 °C)	30
18	**1Dy** (0.5%)	26
19	**1Dy** (2.5%)	62
20	**1Dy** (5.0%)	17

[a] Reaction conditions: indole **2a** (0.50 mmol), *trans*-β-nitrostyrene **3a** (0.50 mmol) in 3 mL of EtOH under 1.0 mol % **1Ln** complexes; [b] Isolated yield by column chromatography.

To explore the scope of the reaction, various nitroalkenes were treated with indole (Table 2). In the first experiments *R*′ was aromatic (Table 2, entries 1–8). Several catalytic systems gave slightly lower yields due to the electronic effect of *para* substitution of the phenyl group of aromatic nitroalkenes. In all these cases, very good yields were obtained, ranging from 92% for the 4-fluoro substrate **4d** to 98% for the tolyl substituted compound **4b**. A slight improvement of the yield up to 99% was observed by use of a heteroaromatic nitroalkene bearing a furan substituent (entry 8). The effect of substitution of the indole is also shown in Table 2 (entries 9–15). The substituent at position 5 of the indole had little effect on yield except for the electron-drawing group (–NO_2) (Table 2, entry 12).

Table 2. Scope of the Friedel–Crafts (FC) alkylation of Indoles with various nitro-styrenes catalysed by **1Dy** [a].



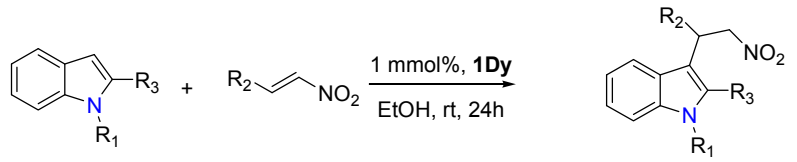
2 **3** **4**

Entry	R^1	R^2	Yield (%) [b]
1	H	Ph	99 (**4a**)
2	H	4-Me-Ph	98 (**4b**)
3	H	4-MeO-Ph	96 (**4c**)
4	H	4-F-Ph	92 (**4d**)
5	H	4-Br-Ph	94 (**4e**)
6	H	2-furan	99 (**4f**)
7	OMe	Ph	97 (**4g**)
8	Br	Ph	95 (**4h**)
9	I	Ph	94 (**4i**)
10	NO_2	Ph	76 (**4j**)
11	$OCH_2C_6H_5$	Ph	96 (**4k**)
12	OMe	2-furan	98 (**4l**)
13	Br	2-furan	95 (**4m**)
14	$OCH_2C_6H_5$	2-furan	96 (**4n**)
15	I	2-furan	95 (**4o**)

[a] Reaction conditions: indole **2** (0.50 mmol) with *trans*-β-nitrostyrene **3** (0.50 mmol) in 3 mL of EtOH under 1.0 mol % **1Dy** complex; [b] Isolated yield by column chromatography.

Further, we investigated the reaction of *N*-alkylated and 2-methyl indole with various nitrostyrenes. The results are summarized in Table 3. The products were isolated in good to excellent yields (Table 3, entries 1–10). A change of the substituent at the nitrogen atom in **5**, and at position 2 of the indole did not show any profound effect on the yield of the desired product (99%, Table 3, entries 1 and 6). Compound **6h** was characterized via single crystal X-ray crystallography (see Figure S1).

Table 3. Friedel–Crafts Alkylation of *N*-alkylated and 2-methyl Indoles with Various Nitroalkenes [a].

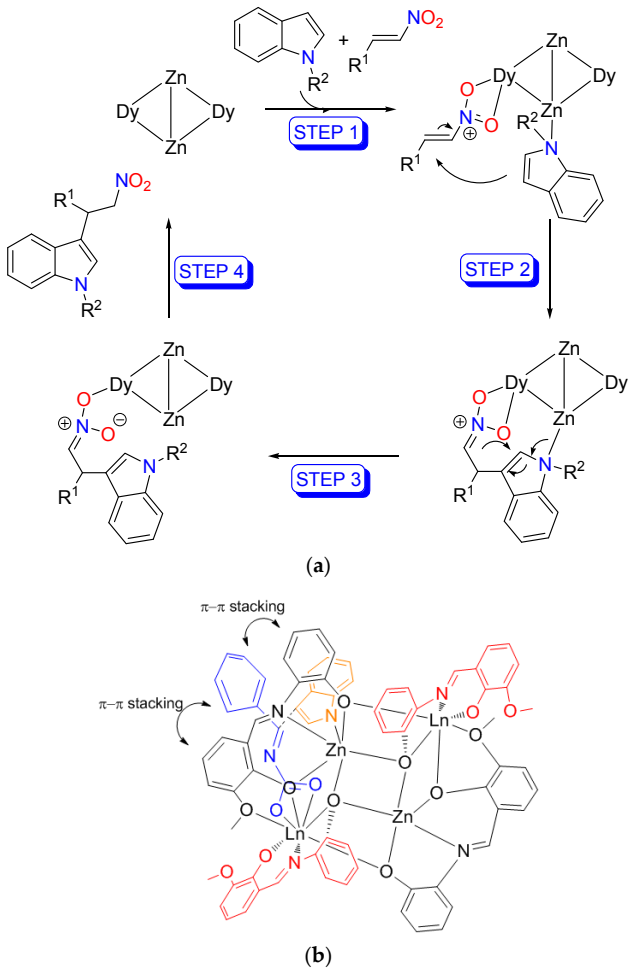


5 **3** **6**

Entry	R^1	R^3	R^2	Yield (%) [b]
1	CH_3	H	Ph	99 (**6a**)
2	CH_3	H	4-MeO-Ph	99 (**6b**)
3	CH_3	H	4-F-Ph	93 (**6c**)
4	CH_3	H	4-Br-Ph	95 (**6d**)
5	CH_3	H	2-furanyl	99 (**6e**)
6	H	CH_3	Ph	99 (**6f**)
7	H	CH_3	4-F-Ph	94 (**6g**)
8	H	CH_3	4-Br-Ph	96 (**6h**)
9	H	CH_3	2-furanyl	99 (**6i**)
10	H	CH_3	4-Me-Ph	98 (**6j**)

[a] Reaction conditions: indole 5 (0.3 mmol), *trans*-β-nitrostyrene 3 (0.3 mmol), 3 mL of EtOH, 1.0 mol % 1Dy complex; [b] Isolated yield by column chromatography.

The substrate binding of *trans*-β-nitrostyrene **3a** by **1Dy** was investigated by UV-Vis spectroscopy in a water/ethanol solution. A 0.1 mM solution *trans*-β-nitrostyrene **3a** exhibited a strong absorption at 320 nm. The **1Dy** was added to the solution and absorption was recorded over 3 h with 5 min intervals between measurements. It was observed (Figure S2) that the intensities of the peak at 320 nm gradually decreased. The quenching of band may be attributed to the bonding of nitrostyrene with **1Dy** through weak Van der Waals interactions. Similar quenching was observed with the indole substrate (Figure S3), indicating the binding behaviour of both substrates to **1Dy**. Thus both substrates can be activated after coordination with the two metal centres in **1Dy** which favours the conjugate addition of the nucleophiles. Similar studies were conducted with $Zn(OTf)_2$ and $Dy(OTf)_3$ to determine the preference of each substrate for the Ln^{III} or Zn^{II} metal centres. In **3a** a greater rate of quenching with $Dy(OTf)_3$ than $Zn(OTf)_2$ is shown, whereas with **2a** the rates are similar. This may suggest that **3a** preferentially binds to the Dy^{III} centre. The **1Dy** catalyst for both substrates demonstrates a greater rate of quenching than either $Zn(OTf)_2$ or $Dy(OTf)_2$, perhaps indicating a stronger interaction with the metal centres in tandem. Based on the above results and the crystal structure of **1Dy** [59] in which a nitrate group chelates to Dy (*trans*-β-nitrostyrene can be considered as an alternative to nitrate), a plausible mechanism and transition state can be proposed shown in Scheme 2. We envision that the nitroalkenes are activated by chelation to Dy^{III} [44] and π–π stacking between the phenyl group of the coordinating ligand L and the phenyl group of nitroalkenes. In addition, the indole substrate will bond to the Zn^{II} through the nitrogen atom and bring the two organic moieties efficiently close to favour the formation of the alkylated product.



(**a**)

(**b**)

Scheme 2. (**a**) A plausible mechanism for the FC alkylation; (**b**) Proposed transition state model of catalyst.

3. Discussion

We report herein, for the first time, a highly efficient, tetranuclear **3d/4f** catalytic system for the FC alkylation of indoles with nitroalkenes. The reaction performs very well over a range of nitroalkenes and indoles, especially those with substituents in the para position. Products are obtained with a yield of up to 98% at room temperature and with only 1% catalyst loading, showcasing the efficacy of these catalytic species. Further exploration of the mechanism of this specific reaction, the involvement of chiral ligands for the synthesis of **3d/4f** CCs and their employment in other asymmetric reactions is currently under way in our laboratory.

4. Materials and Methods

All chemicals and solvents were purchased from Sigma Aldrich, S.D. Fine Chemicals, and commercial suppliers. The progress of the reaction was monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 plates. Products were purified by column chromatography on silica gel (60–120 mesh). NMR spectra were collected using a Bruker Advance III HD 500 MHz Spectrometer. The ^{1}H and ^{13}C NMR spectroscopic data were analysed with a 500 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. The coupling constants (*J*) are reported in Hz, and the splitting patterns of the proton signals are described as s (singlet), d (doublet), t (triplet), and m (multiplet).

4.1. Synthesis of Catalysts

All CCs were synthesised according to the literature [59].

4.2. General Procedure for the Friedel–Craft Reaction

All experiments were carried out in the open atmosphere and on a mmol scale. A 10 mL round bottom flask was charged with catalyst **1Dy** (1.0 mol %), nitrostyrene (0.5–0.3 mmol), indole (0.5–0.3 mmol). Solvent (3 mL) was added and the reaction mixture was stirred for 24 h at room temperature. The product was purified by silica gel column chromatography.

4.3. Single Crystal X-Ray Structure Determinations

Crystals suitable for single crystal X-ray diffraction analyses were obtained for compound **6h**. Preliminary data on the space group and unit cell dimensions, as well as intensity data, were collected on an Agilent Xcalibur Eos Gemini Ultra diffractometer with a CCD plate detector, under a flow of nitrogen gas, at 173(2) K using Mo Kα radiation (λ = 0.71073 Å). CRYSALIS CCD and RED software Reflection intensities were corrected for absorption by the multi-scan method. Structure solution and refinement were accomplished using Olex2 [61], solved using either Superflip [62] and refined with SHELXL [63]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were geometrically fixed and allowed to refine using the riding model. Geometric/crystallographic calculations were performed using Olex2 [61], package; graphics were prepared with Crystal Maker [64]. CCDC 1482790.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/6/9/140/s1.

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Author Contributions: P.K. and G.E.K. conceived and designed the experiments; P.K., K.G., S.L. and S.I.S. performed the experiments. G.E.K. Analysed the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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